

An Equation of State for the Hard Sphere Chain Fluids Based on the Thermodynamic Perturbation Theory of Sequential Polymerization

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New equations of state for the jointed hard sphere chain fluids are developed. The equations of state are based on thermodynamic perturbation theory. The new equations of state use the contact values of the radial distribution function (RDF) for monomer-dimer mixtures, which are derived from the multidensity Ornstein-Zernike theory. These RDFs are composed of a monomer reference term, the Carnahan-Starling or the Percus-Yevick expressions, and an additional bond contribution. We compare these expressions for RDFs with the Monte Carlo simulation results for monomer-dimer mixture fluids. We also compare the resulting equations of state with the simulation results for the compressibility factors of the hard sphere chain fluids. The predictions are in a good agreement with simulation data especially at high densities.

We then extend these equations of state to real fluids. In order to calculate the phase equilibrium properties of non-associating chain fluids, a dispersion contribution is added to the repulsive hard-chain reference term. This dispersion term is constructed by combining exact analytical expressions and rigorous simulation data for the compressibility factors of square-well monomer fluids. With the new equations of state of chain fluids supplemented with the dispersion term, the vapor pressures and the coexisting densities of several real fluids are calculated. Also, we find a good agreement between the predictions of the theories and experimental data.